Proceedings of the American Academy of Arts and Sciences

VOL. 76, NO. 1, P. 1–24—FEBRUARY, 1945

THE COMPRESSION OF TWENTY-ONE HALOGEN COMPOUNDS AND ELEVEN OTHER SIMPLE SUBSTANCES TO 100,000 kg/cm²

BY P. W. BRIDGMAN

THE COMPRESSION OF SIXTY-ONE SOLID SUBSTANCES TO 25,000 kg/cm², DETERMINED BY A NEW RAPID METHOD

BY P. W. BRIDGMAN

THE COMPRESSION OF TWENTY-ONE HALOGEN COMPOUNDS AND ELEVEN OTHER SIMPLE SUBSTANCES TO 100,000 kg/cm²

By P. W. Bridgman

Presented Oct. 11, 1944. Received Oct. 17, 1944.

Contents

Introduction 1
Method of Measurement and Calculation 1
Experimental Details 2
Discussion of Results 4

Introduction

In this paper the method previously used[1] in determining the compressions of seventeen elements to 100,000 kg/cm² is extended to a determination of the twenty-one halogen compounds of sodium, potassium, rubidium, caesium, silver, thallium, and ammonium, of the corresponding seven nitrates, of sulfur, of silver bromate, of metallic lead both in the massive and finely powdered condition, and to a redetermination of the compression of metallic indium.

The measurements on sulfur and all the salts except NH_4NO_3 were made in 1941 and early 1942, and have been waiting since for an opportunity for publication. The measurements on NH_4NO_3, lead, and indium were made early in 1944, when opportunity was found to resume measurements. The apparatus had been left untouched in the interval, and on resumption of work functioned at once, with no important alteration in any of the constants, except for one matter to be mentioned presently.

In addition to the measurements recorded here, data were also obtained for the compressions of arsenic, and of lead sulfide, selenide, and telluride. The frictional resistance to the motion of the piston offered by these hard substances resulted in so great difference between the displacements with increasing and decreasing pressure that it did not seem worth while to subject the measurements to calculation. It can be stated, however, that no new transitions were found in the range above 50,000; the known transitions of the selenide and telluride below 50,000 were again encountered. It will probably be possible to make satisfactory measurements on substances as hard as these by a modification in technique which has been sufficiently used to show its promise. This consists in enclosing the substance in a thin capsule of indium, by which the stress on the outside of the specimen is reduced to an approximate hydrostatic pressure. Any measurements by this technique will be reserved for a future communication.

Method of Measurement and Calculation

As compared with the previous work already described in full detail, little change was made in the experimental technique. A revised method of calculation was adopted, however. It will be recalled that the method is a differential one, in which the piston displacement is determined as a function of pressure when the piezometer is filled with the substance under investigation and when filled with gold, it being assumed that the compression of gold is known. In any single run the measured piston displacement is a function not only of the pressure prevailing inside the high pressure piezometer, but also of the hydrostatic pressure in the surrounding liquid, of the pressure driving the piston by which this pressure is produced (that is, it is a function of the friction on the ram of the hydraulic press), and of the external pressure applied to the cylinder of the 30,000 apparatus to prevent it from bursting, the effect of this external pressure being to lengthen the 30,000 cylinder and give an apparent component to the displacement of the piston of the 100,000 piezometer. In the previous method of calculation mean values were applied for these various disturbing effects, the corrections being calculated at the extreme points on the basis of the average of many runs and the corrections for intermediate points were determined by linear interpolation. The new method of calculation was considerably more elaborate in that the three corrections were calculated in detail at every point from the various actual readings at that point. In general, the new procedure gives lower

values for the volume decrements, the decrease being confined almost entirely to the lower end of the pressure range from 25,000 to 50,000 kg/cm². The presumptive superiority of the new and more elaborate method is established by the fact that the revised method gives better agreement with the previous measurements[2] on the halogen compounds in the common range. These compounds had been previously measured in the range from atmospheric pressure up to 50,000 kg/cm².

A fundamental datum necessary in the calculations is the compression at 25,000 kg/cm², this being the initial pressure of these measurements. The compressions at 25,000 of the halogen compounds had been previously determined, as just mentioned, but no such information was in existence for the nitrates or $AgBrO_3$. Independent measurements were therefore made of the compression of these substances to 25,000 kg/cm². These were made by a new method with a new apparatus which permits rapid measurements of sufficient accuracy. The measurements will be described in the paper[3] immediately following; only the results will be used here.

An improvement has been introduced in the method for determining the compression coëfficient of the compressometer which permits its rapid determination, while the compressometer is mounted in the 30,000 apparatus *in situ* ready for the measurements to 100,000. The constant freshly determined by this method was a few per cent lower than in the original determination by the former method several years ago.

The difficulty on resuming measurements referred to at the end of the second paragraph of the introduction was the following. A new manipulative trick which much facilitated assembly was adopted on resumption of work; this consisted in holding one of the loose carboloy plattens in position with a minute gob of wax. Many irregular results, including spurious polymorphic transitions, were traced after much time and effort to the account of the wax. At low pressures the wax dissolves in the isopentane by which pressure is transmitted and is carried in solution between the carboloy platten and the grid with which the compressive stress on the piston is measured. The first few thousand atmospheres precipitates this wax in a thin film and freezes it hard; later, when the pressure in the 100,000 piezometer has reached something over 50,000, it is plastically squeezed out in the solid condition, resulting in a spuriously large piston displacement which may simulate a transition. The remedy is scrupulously to free all internal parts of the assembly from any grease or similar substance.

Most of the substances were independently measured with two different piezometers, and the final results are the mean of two runs. Seven different piezometers were used in all, sufficient to permit definite conclusions as to the best grade of carboloy to be used in their construction. Five of these piezometers were made of carboloy no. 905, the grade which was found to be the most successful for the pistons in the measurements of volume changes already published up to 50,000 kg/cm². These five piezometers broke after respectively seven, twelve, seven, six, and five exposures to 100,000 kg/cm². Of the two remaining piezometers, one was of grade no. 55A and the other of grade no. 779. The first of these has at the date of writing survived 55 exposures without fracture and the second 35. The inferiority of grade no. 905 for this purpose is manifest.

Experimental Details

The material used in these measurements was, with few exceptions, the same as that used in previous measurements either of the compressions to 50,000, or in explorations for polymorphic transitions to 50,000,[4] and has already been described in previous papers. My old stock of single crystal NaI was exhausted and the material used here was obtained from the stock room of the Harvard Chemical Laboratory, melted in platinum, and the clear parts of the solidified product selected. NH_4Cl and NH_4Br were also fresh material from the stock of the chemical laboratory, used directly without further purification. The lead was special lead of 99.9999 per cent purity, as in the previous paper.

There follow now the pertinent details connected with the measurements of the individual substances. In the final results the mean of two independent runs was usually used, and this mean was smoothed so as to give smooth first differences over the entire pressure range from zero up, making a compromise between the present and former determinations in the common range.

In Table I certain data are given which will permit an estimate of the internal consistency of the measurements. This table gives the difference between the volume decrement at 100,000 kg/cm² as determined with either of the

TABLE I

Substance	Difference between mean $\Delta V/V_0$ at 100,000 and individual measurements	Preceding column as fraction of maximum $\Delta V/V_0$	Difference between former $\Delta V/V_0$ at 50,000 and new smoothed result
NaCl	.007	.033	+.004
NaBr	.007	.032	+.007
NaI	.011	.041	+.011
KCl	.008	.025	+.004
KBr	.014	.041	+.009
KI	.010	.029	+.007
RbCl	.000	.000	+.015
RbBr	.006	.017	+.012
RbI	.014	.035	+.016
CsCl	.005	.021	+.006
CsBr	.007	.026	+.011
CsI	.012	.041	+.005
AgCl	.000	.000	+.006
AgBr	.005	.030	+.002
AgI	——	——	+.010
TlCl	.003	.014	+.013
TlBr	.010	.045	+.014
TlI	.011	.043	+.022
NH_4Cl	.010	.044	+.008
NH_4Br	.010	.040	+.002
NH_4I	.017	.045	+.005
S	——	——	+.012
Pb	.001$_4$	.010	——

two individual piezometers and the mean of the two, both as absolute volume decrement, the volume at atmospheric pressure being taken as unity, and as the fraction which the difference is of the total volume decrement at 100,000. The discrepancy between the two runs was in nearly all cases a maximum at 100,000. Of the substances listed in Table I, measurements were made on AgI with only one piezometer, and although measurements were made on NH_4I with two piezometers, the values obtained with one of them differed so much from the values previously found up to 50,000 that they were discarded and the values listed later in Table IV are based on those obtained with the other piezometer only. The difficulty with NH_4I is to a large extent characteristic of the particular material. This has a large polymorphic transition at a pressure of only a few hundred kilograms; the volume change is so large that it cannot possibly be compensated by the differential compressibility of steel and carboloy, as described in the previous paper, with the result that opportunity is afforded for the capricious trapping of liquid inside the solid resulting in too large compressions. The only way of telling whether this capricious trapping has occurred is by the internal consistency of the results; the discarding of markedly discordant runs would seem to be justified under the conditions.

The agreement of the two runs for lead and indium is, both absolutely and fractionally, better than on the average for the salts, in spite of the fact that the absolute magnitude of the volume decrement is greater for the salts. This is without doubt a consequence of the much greater softness of the two metals, resulting in better agreement between the displacements with increasing and decreasing pressure. Measurements were made on both lead and indium in the new apparatus for 25,000. For indium there are previous measurements for comparison[5] both in the range up to 50,000, and also to 100,000, computed by the old method. Compared with previous results, the new results are somewhat higher in the neighborhood of 50,000 than the previous results with the 50,000 apparatus, and somewhat lower than the previous results to 100,000 over the entire range. These differences are in the usual direction.

Measurements were made with only one piezometer on each of the nitrates; this was the same piezometer for all. The difference between increasing and decreasing pressure was about the same for the nitrates as for the halogen compounds, and the probable accuracy should be about the same. There are no previous measurements on the compression of nitrates to 50,000 for comparison.

Table I also lists the discrepancy between the values formerly obtained for the volume decrements at 50,000 and the values now adopted on the basis of the smoothing process over the entire range. This discrepancy is always of the same sign; that is, the value adopted here for the volume decrement is consistently greater at 50,000 than the value previously found from the measurements in the range from atmospheric to 50,000. This indicates a consistent error in the measurements somewhere. It seems probable that this consistent error is in the previous measurements to 50,000 and is connected with the fact that we are here dealing with the end of the range. It is always more difficult to get reliable measurements up to the end of the range than in the middle of the range. The sign of the discrepancy is doubtless associated with the friction, which of course is greatest at the top of the range.

The smoothed values adopted for 50,000 are also consistently less than those which would have been indicated by the measurements of this paper for the range 25,000 to 100,000. We are here dealing with the lower end of the pressure range and therefore probably with the inverse of the

effect above. That is, this method tends to give too large volume decrements at the lower end of the range and too small decrements at the upper end of the range. The accuracy of the present measurements is probably greatest in the range from 50,000 to 75,000.

Discussion of Results

The numerical values of the volume decrements, in terms of the volume at atmospheric pressure as unity, are given in Tables II to VI and are plotted in Figures 1 to 4.

No elaborate discussion of these data will be attempted. Qualitatively the behavior in the range from 50,000 to 100,000 is merely a continuation of that already found in the range below 50,000. There is very little tendency for the curves of volume decrement to cross above 50,000, and the few examples of it may be due to experimental error. In a general way the atomic contributions to the volume decrements are distinctly recognizable and are the most

TABLE II

$\Delta V/V_0$ of Various Chlorides

Pressure kg/cm²	NaCl	KCl	RbCl	CsCl	AgCl	TlCl	NH_4Cl
10,000	.038	.048	.188[b]	.048	.021	.038	.049
20,000	.068	.084	.219	.086	.040	.071	.082
30,000	.093	.223[a]	.246	.118	.058	.099	.109
40,000	.115	.244	.270	.144	.074	.123	.133
50,000	.135	.262	.292	.166	.090	.144	.154
60,000	.152	.277	.311	.184	.104	.162	.172
70,000	.168	.290	.327	.199	.117	.177	.188
80,000	.183	.302	.341	.212	.129	.191	.202
90,000	.197	.312	.353	.223	.140	.202	.215
100,000	.210	.321	.364	.233	.165[c]	.213	.227

[a] Transition at 20,060; $\Delta V/V_0$'s at transition .085 and .197
[b] Transition at 5,000; $\Delta V/V_0$'s at transition .030 and .170
[c] Transition at 90,000; $\Delta V/V_0$'s at transition .140 and .156

TABLE III

$\Delta V/V_0$ of Various Bromides

Pressure kg/cm²	NaBr	KBr	RbBr	CsBr	AgBr	TlBr	NH_4Br
10,000	.043	.055	.188[b]	.053	.022	.043	.049
20,000	.078	.199[a]	.221	.095	.041	.077	.088
30,000	.107	.229	.250	.130	.059	.106	.120
40,000	.132	.254	.275	.160	.075	.131	.147
50,000	.153	.274	.297	.186	.091	.152	.170
60,000	.171	.291	.315	.208	.106	.170	.189
70,000	.186	.305	.330	.227	.120	.186	.205
80,000	.199	.317	.343	.243	.133	.200	.219
90,000	.211	.327	.354	.258	.157[c]	.212	.232
100,000	.222	.336	.364	.272	.169	.223	.244

[a] Transition at 18,400; $\Delta V/V_0$'s at transition .088 and .193
[b] Transition at 4,600; $\Delta V/V_0$'s at transition .033 and .166
[c] Transition at 86,000; $\Delta V/V_0$'s at transition .141 and .152

TABLE IV

$\Delta V/V_0$ of Various Iodides

Pressure kg/cm²	NaI	KI	RbI	CsI	AgI	TlI	NH_4I
10,000	.056	.065	.192[b]	.065	.189[c]	.050	.192[d]
20,000	.098	.197[a]	.235	.113	.209	.090	.230
30,000	.132	.230	.271	.151	.228	.123	.258
40,000	.160	.257	.301	.182	.246	.152	.282
50,000	.184	.279	.326	.208	.263	.177	.302
60,000	.205	.298	.346	.230	.278	.198	.320
70,000	.223	.314	.362	.249	.292	.216	.335
80,000	.239	.327	.376	.266	.305	.232	.350
90,000	.253	.338	.388	.281	.317	.245	.363
100,000	.266	.348	.398	.294	.328	.256	.376

[a] Transition at 18,200; ΔVV_0's at transition .105 and .190
[b] Transition at 4,050; ΔVV_0's at transition .035 and .161
[c] Transition at 3,000; ΔVV_0's at transition .011 ± & .174
[d] Transition at 560; ΔVV_0's at transition .003 ± & .143

TABLE V

$\Delta V/V_0$ of Various Nitrates

Pressure kg/cm²	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$	$AgNO_3$	$TlNO_3$	NH_4NO_3
10,000	.034	.138[b]	.043	.045	.044[c]	.037	.050
20,000	.062	.169	.079	.083	.077	.068	.086
30,000	.086	.196	.109	.115	.103	.095	.115
40,000	.107	.219	.135	.142	.126	.118	.140
50,000	.127	.238	.157	.165	.146	.137	.162
60,000	.154[a]	.255	.175	.183	.162	.152	.180
70,000	.167	.268	.190	.198	.176	.165	.194
80,000	.180	.280	.202	.210	.188	.176	.206
90,000	.191	.289	.211	.219	.198	.185	.215
100,000	.201	.297	.219	.226	.206	.194	.222

[a] Transition at 55,000; $\Delta V/V_0$'s at transition .136 and .147
[b] Transition at 3,650; $\Delta V/V_0$'s at transition .023 and .113
[c] Transition at 9,500; $\Delta V/V_0$'s at transition .030 and .043

TABLE VI

$\Delta V/V_0$ of Four Miscellaneous Substances

Pressure kg/cm²	$AgBrO_3$	Pb	In	S
10,000	.027	.0215	.0240	.083
20,000	.050	.0410	.0442	.131
30,000	.071	.0587	.0619	.163
40,000	.088	.0747	.0781	.188
50,000	.104	.0892	.0932	.208
60,000	.117	.1024	.1072	.225
70,000	.129	.1145	.1202	.240
80,000	.138	.1255	.1324	.253
90,000	.147	.1356	.1439	.264
100,000	.154	.1449	.1549	.274

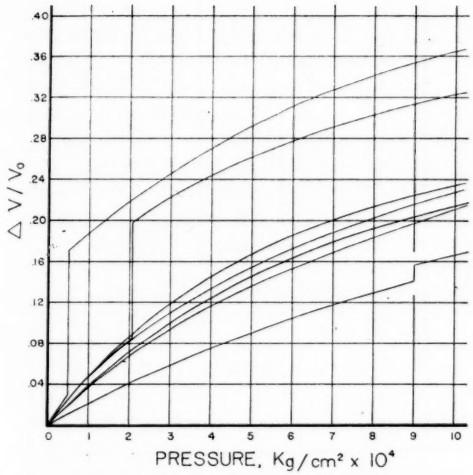

FIGURE 1. The volume decrements of the chlorides as a function of pressure. The order of the curves at 100,000 kg/cm², reading from top down, is: Rb, K, Cs, NH_4, Tl, Na, and Ag.

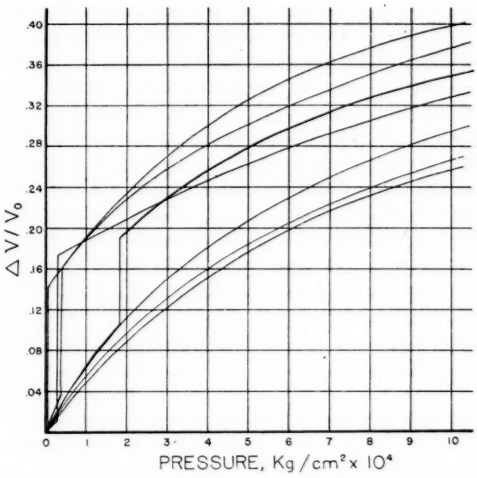

FIGURE 3. The volume decrements of the iodides as a function of pressure. The order of the curves at 100,000 kg/cm², reading from top down, is: Rb, NH_4, K, Ag, Cs, Na, and Tl.

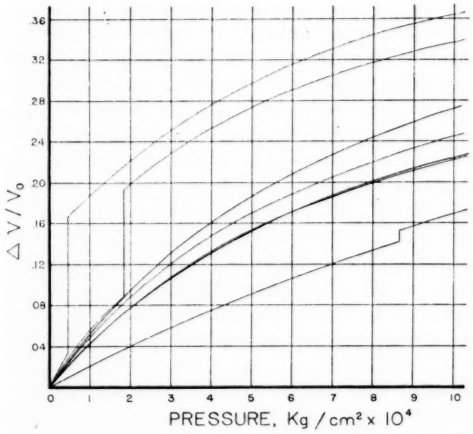

FIGURE 2. The volume decrements of the bromides as a function of pressure. The order of the curves at 100,000 kg/cm², reading from top down, is: Rb, K, Cs, NH_4, Tl, Na, and Ag.

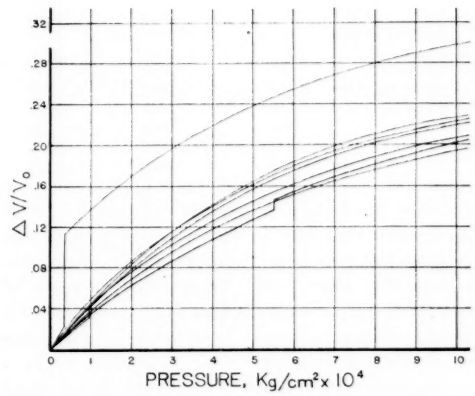

FIGURE 4. The volume decrements of the nitrates as a function of pressure. The order of the curves at 100,000 kg/cm², reading from top down, is: K, Cs, NH_4, Rb, Ag, Na, and Tl.

important factor in determining compression at these high pressures. Disregarding the effect of polymorphic transition, and other things being equal, the compression increases on passing from chloride to bromide to iodide. The nitrates are about as compressible as the corresponding chlorides. With regard to the atom of the metal, the compression increases in the series sodium, potassium, rubidium, and caesium. The compounds of thallium in general show about the same compression as the corresponding sodium compounds, and the compounds of ammonium the same as those of potassium or rubidium. The compounds of silver are distinctly less compressible than those of any of the other metals just enumerated.

The falling off in compressibility with increasing pressure may be exhibited by comparing the volume decrement for the interval atmospheric to 50,000 with that for the interval 50,000 to 100,000. These values are listed in Table VII,

TABLE VII

COMPARISON OF VOLUME DECREMENTS AT LOW AND HIGH PRESSURES

Substance	$\Delta V/V_0$ 0–50,000	$\Delta V/V_0$ 50,000–100,000	Ratio
NaCl	.135	.075	1.80
CsCl	.166	.067	2.48
TlCl	.144	.069	2.08
NH_4Cl	.154	.073	2.11
NaBr	.153	.069	2.22
CsBr	.186	.086	2.16
TlBr	.152	.071	2.13
NH_4Br	.170	.074	2.29
NaI	.184	.082	2.24
CsI	.208	.086	2.42
TlI	.177	.079	2.24
$RbNO_3$	.157	.062	2.53
$CsNO_3$	.165	.061	2.71
$TlNO_3$	137	.057	2.41
NH_4NO_3	.162	.061	2.66
$AgBrO_3$	.104	.050	2.08
Pb	.089	.056	1.60
In	.093	.062	1.52
S	.208	.066	3.14

and are plotted in Figure 5. Figure 5 clearly shows the well known fact that in general the greater the absolute compressibility of a substance the more rapid its relative decrease of compressibility with increasing pressure. It would, in fact, be surprising if something like this were not approximately the case, this being a geometrical consequence of the fact that an upper limit to the volume decrement is unity, negative volumes being meaningless. Figure 5 also brings out another general tendency, namely that other things being equal the substance with the more complicated atomic structure experiences the

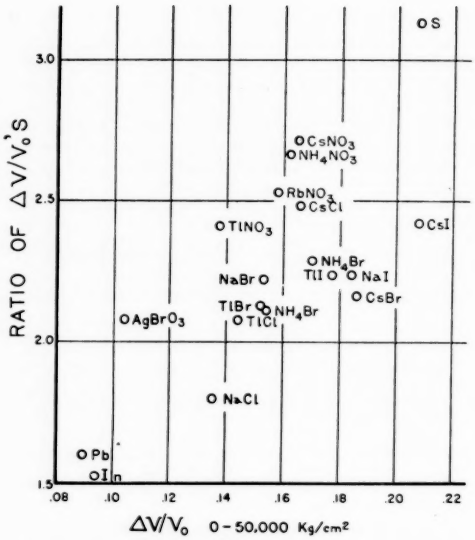

FIGURE 5. The ratio of the volume decrement 0 to 50,000 kg/cm² to the decrement 50,000 to 100,000 kg/cm² plotted against the volume decrement 0 to 50,000 kg/cm².

greatest relative decrease of compressibility with increasing pressure. This again would be expected on rather general grounds. The more complicated structure may be expected to have more internal vacancies or more "slack" to be taken out by the initial application of pressure. In this respect the solid with complicated structure approaches more closely to a liquid, in which there is a large amount of internal slack and a rapid initial decrease of compressibility with increasing pressure.

Only three examples of new polymorphic forms were found: $NaNO_3$, AgCl, and AgBr. It is perhaps surprising that not more were found, although in explanation it is to be commented that already at low pressures most of these substances must have already acquired about their maximum simplicity and symmetry of structure. It is probable that the transitions of AgCl and AgBr are from the face centered lattice, which is the stable form at atmospheric pressure, to the body centered lattice, in analogy with the transitions of the potassium and rubidium halides. It is of some interest that no transition was found for the sodium halides. A formal extrapolation of the results already found for the halides of rubidium and potassium might lead to the expectation of transitions of the sodium salts in the

new range. However, a careful calculation of the probable energy relations by Dr. Jacobs[6] has indicated that the probability of the transition fades out of the picture somewhere between potassium and sodium, and these experimental results support his conclusion.

There does not seem to be any simple method of guessing what the type of transition is for $NaNO_3$, the nitrates exhibiting a number of possibilities in the way of transition.

On the basis of previous measurements[7] it might have been expected that transitions would have been found for rubidium, caesium, and silver nitrates. However, if the previous work is consulted it will be found that the transition of $CsNO_3$, which occurs in the neighborhood of 30,000, was getting so sluggish that it could not be picked up even with the former apparatus at temperatures below 125°. $RbNO_3$ similarly, which according to the former measurements has a transition at room temperature in the neighborhood of 17,000 kg/cm², is nevertheless so sluggish at this temperature that the band of indifference was 14,000 kg/cm² wide. It is therefore probable that the transitions of both $CsNO_3$ and $RbNO_3$ were totally suppressed in this work, and that the volume decrements listed here apply to the ordinary modifications, compressed far into their regions of thermodynamic instability. $AgNO_3$, on the other hand, according to previous work has a couple of transitions between 30,000 and 45,000 which might have been picked up. It is to be remarked, however, that the first of these transitions, from II to III, is sluggish, and may have been suppressed, the much greater speed and the much smaller quantity of substance in these experiments both being factors favoring suppression of the transition. It is true that the second transition found before, from III to IV, was not sluggish at room temperature, but if the transition from II to III had not previously occurred we would be concerned at high pressures with the transition II to IV, instead of III to IV, and there is no basis for judging whether the former transition would be sluggish or not. The probability is, therefore, that all transitions were suppressed, and that the volume decrements of Table V are the decrements for phase II. Taken altogether, these results give increased probability to the correctness of Tammann's thesis, for which there was already much favorable evidence, that the probability of transition to the thermodynamically stable modification passes through a maximum and then decreases as pressure increases along an isotherm away from the point of reversible transition.

It is a pleasure to acknowledge the skillful assistance of my mechanic Mr. Charles E. Chase.

RESEARCH LABORATORY OF PHYSICS,
Harvard University, Cambridge, Mass.

REFERENCES

[1] P. W. Bridgman, Phys. Rev. 60, 351–354, 1941.
Proc. Amer. Acad. 74, 425–440, 1942.
[2] P. W. Bridgman, Proc. Amer. Acad. 74, 21–51, 1940.
[3] P. W. Bridgman, Proc. Amer. Acad. (to be supplied in proof)
[4] P. W. Bridgman, Proc. Amer. Acad. 72, 45–135, 1937.
[5] Reference 2, p. 31, and second reference under 1, p. 434.
[6] R. B. Jacobs, Phys. Rev. 54, 468–474, 1938.
[7] P. W. Bridgman, Proc. Amer. Acad. 51, 581–625, 1916, and also reference 4, pp. 86 and 87.

THE COMPRESSION OF SIXTY-ONE SOLID SUBSTANCES TO 25,000 kg/cm², DETERMINED BY A NEW RAPID METHOD

By P. W. Bridgman

Presented Oct. 11, 1944. Received Oct. 17, 1944.

Contents

Introduction 9
Apparatus and Method 9
Detailed Results 14
1. Elements 14
Thallium 14
Arsenic 15
Cadmium 15
Indium 16
Lead 16
Carbon (graphite) 17
2. Inorganic Salts 17
A. Univalent Nitrates 17
B. Certain Halogenates and Perhalogenates 18
3. Organic Solids 19
A. Definite Compounds 19
B. Synthetic and Natural Rubbers 21

Introduction

In the following, a new apparatus is described by which the cubic compression of solid substances may be rapidly determined in the pressure range from atmospheric to 25,000 kg/cm² at room temperature, and the results obtained with it are presented for 6 elements, 26 salts, 15 organic solids, and 14 artificial and natural rubbers. The apparatus operates on about 0.1 cm³ of material, requires two hours or less for the complete run, including assembly, and disassembly ready for the next run, with 30 readings uniformly spaced over the pressure range. The individual points lie smoothly on a curve within 1 part in 2000 of the initial volume or better, depending on the nature of the material, with correspondingly greater accuracy in the mean curve.

Apparatus and Method

The method is a development of the method previously used[1] for the determination of compressions and polymorphic transitions to 50,000 kg/cm². By this method, the material, enclosed in a sheath of a soft metal, usually indium, in order to ensure that the stress should be approximately hydrostatic, was placed in a steel container with an external conical surface fitting a steel sleeve, so designed that when the internal pressure increased the external pressure simultaneously increased, thus resisting the tendency to fracture. The volume compression was determined from the motion of the piston with which pressure was generated. The reduction of the measured piston displacement to volume decrement involved a number of corrections, which were somewhat in doubt because of friction and hysteresis. The pressure range was so high that the containers were subject to slow creep in dimensions, which always eventually resulted in fracture after anywhere from 10 to 100 applications of pressure.

The new and modified method in the first place restricts the pressure to one half the former range, with the object of avoiding creep and fracture and permitting the indefinite use of the apparatus. This appears to have been successful, and to date some 200 applications of 25,000 have been made with no fracture of any part of the apparatus and no measurable change of any dimension. The corrections, furthermore, are much simplified and minimized by so designing the apparatus that the change of cross sectional area of the container under internal pressure is small, leaving as the one most important outstanding correction one for the longitudinal compression of the carboloy pistons.

The apparatus is shown in detail in Figure 1. It is mounted on the same "tandem" hydraulic press that was previously used in the measurements to 50,000. This press comprises in the first place a 6-inch plunger, by which the pressure vessel is pushed as a whole into its conical sleeve so as to generate the external pressure resisting fracture. Riding on the 6-inch piston is a 3.5 inch piston by which pressure is exerted on the inside of the high pressure chamber. The core of the high pressure vessel itself is made of car-

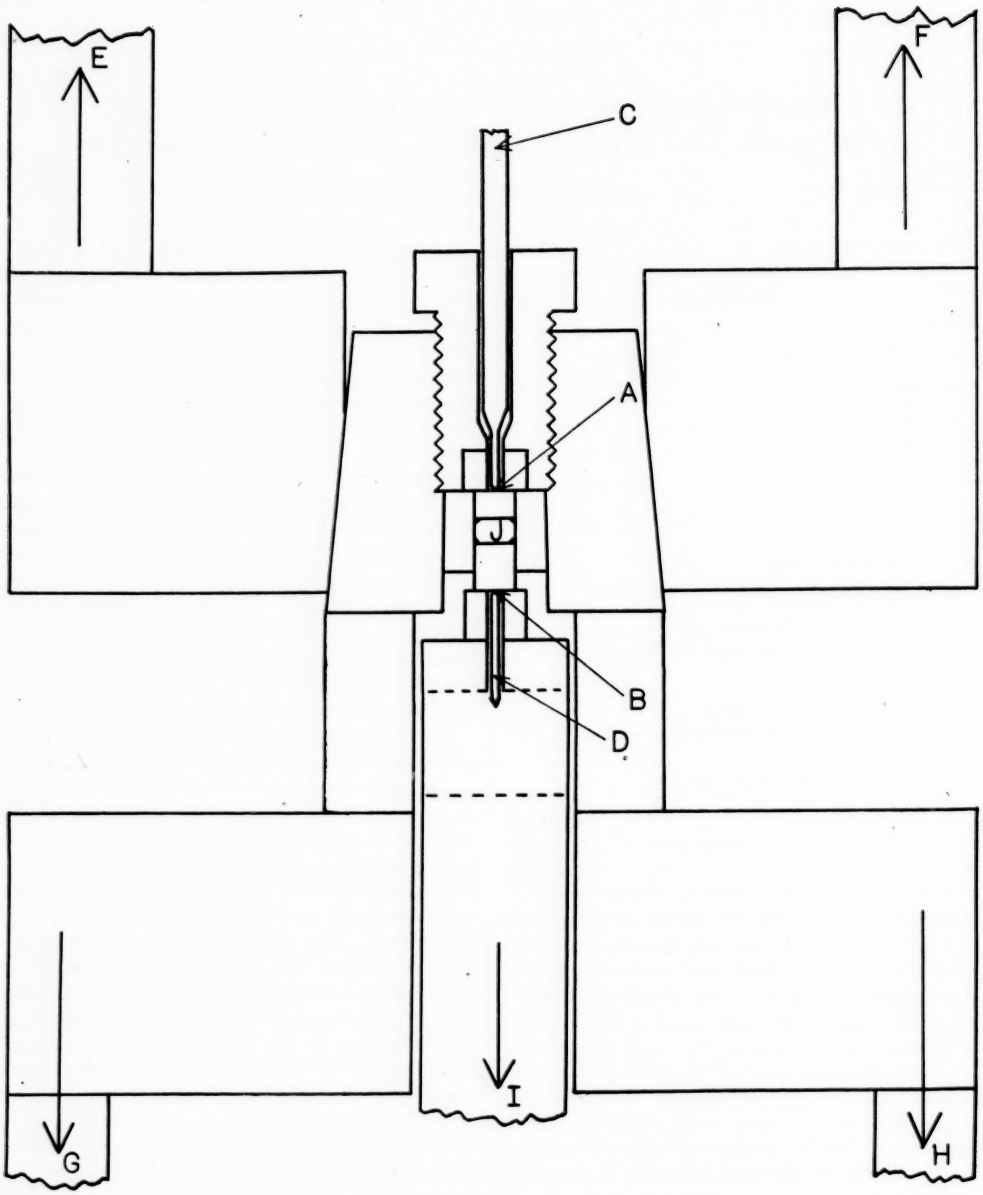

FIGURE 1. General assembly of compressibility apparatus. The charge whose compression is to be measured is shown at J. The relative motion between the points A and B is taken off by means of the feeler rods C and D and a yoke and 1/10,000 gauge (not shown). The compression member I is actuated by the ram of the 3.5 inch press (not shown), and the conical vessel is pushed into its supporting collar by means of G and H actuated by the ram of the 6 inch press (not shown). The members E and F transmit the total thrust to the top platten of the tandem press (not shown).

boloy, grade no. 905, 0.47 inches long and 0.63 inches outside and 0.25 inches inside diameter, ground with a taper of 0.010 inches on its total length, and forced into the surrounding conical steel block to such an extent as to expand the inside of the steel block by 0.004 inch. In operation, the two pistons of the tandem press are both directly connected to the single source of hydraulic pressure, instead of being connected through a multiplying mechanism by which the pressure on the two pistons was previously maintained at a fixed ratio different from unity. In this way operation was simplified and error from friction in the multiplier avoided. The dimensions and angle of the steel block into which the carboloy core was forced were so chosen that the pressure on the outside of the carboloy was automatically maintained at about one quarter of the internal pressure. Under these conditions the internal expansion of the carboloy container keeps pace with the small lateral expansion of the carboloy piston so that the crack around the piston remains of constant size, and the tendency to leak, or the friction with the piston, does not increase. It is to be remarked that apart from the other improvements in design, merely by making the core of carboloy the distortions were cut down to one-third of what they would have been with steel, because of the higher elastic constants of carboloy.

The charge, whose volume compression is to be measured, occupies the central part of the carboloy core, and is approximately 0.125 inches long and 0.250 inches in diameter. These dimensions are a compromise. The longer the charge, the greater the change in length for a given change of pressure, that is, the greater the sensitivity, but on the other hand, the greater the length, the greater the friction and the greater the error from difference between displacements with increasing and decreasing pressure. Theoretically, the ratio of the frictional force to the total compressing force may be made vanishingly small by indefinitely reducing the ratio of the surface on which the friction acts to the area on which the total compressing force acts, that is, by making the charge in the form of an indefinitely thin disc. But in this case the displacements which measure the volume compression also become vanishingly small. The dimensions just mentioned were chosen after some trial as giving a reasonable compromise.

The charge is compressed between two cylindrical carboloy blocks, the upper block in Figure 1 being held rigidly in place against a carboloy anvil inserted into the steel retaining screw, and the other block constituting the compressing piston. The relative displacement of the ends of these two blocks was measured by steel feeler rods reaching in through axial holes in the supporting carboloy anvil blocks as shown, and connected with an Ames 0.0001 inch jeweled gauge. The gauge had been specially selected by the manufacturers from a large number because of its negligibly small calibration errors. The relative displacement, measured in this way, is, except for the distortion of the blocks, the change of length of the charge, and from this, if the change of cross section of the charge is known, the volume decrement of the charge may be at once obtained. The distortion of the blocks consists primarily of a shortening, but superposed on this the faces in contact with the charge may not remain flat. With the dimensions chosen the effect of any warping of the plane ends of the blocks appears to be negligibly small, but the warping becomes relatively more important as the thickness of the charge is made smaller, and eventually would impose a limit, entirely apart from the effect of the decrease of the absolute magnitude of the measured displacement as the disc becomes thinner.

With the actual dimensions of the charge, 0.25 inch diameter and 0.125 inch long, the friction on the walls of the carboloy container generated by the longitudinal motion connected with the compression would have been excessive for most solid substances, so that it was necessary to surround the charge with a sheath of indium, as in previous work. The indium is so soft that it will support only an approximately hydrostatic pressure, thus producing the proper stress system on the charge and at the same time eliminating most of the friction on the walls. The indium, in weighed amount, usually in the neighborhood of 0.140 gm., was formed into a cup shaped sheath in place in the carboloy container with a suitably shaped forming tool, the thick bottom of the cup being in contact with the moving carboloy piston, and the thin edge of the cup being in contact with the stationary carboloy block. (Figure 2.) The solid to be measured was, if originally in the form of powder, formed into a conical slug by compression in a split mold, or, if it was coherent enough, was turned in the lathe from the massive block to such dimensions as to fit the inside of the indium cup. The indium was prevented from leaking past the carboloy pistons

by thin conical steel rings as indicated in the figure. These rings were made initially about 0.001 inch too large in diameter, but because of their thinness they could be seated in position with the exercise of only a moderate force. They were effective in preventing any detectible leak. The quantity of steel in the sealing rings was controlled by weighing, the weight being about 0.015 gm. each. A slight correction was applied for the compression of the rings.

Pressure was applied to the two pistons of the tandem press through the medium of ordinary

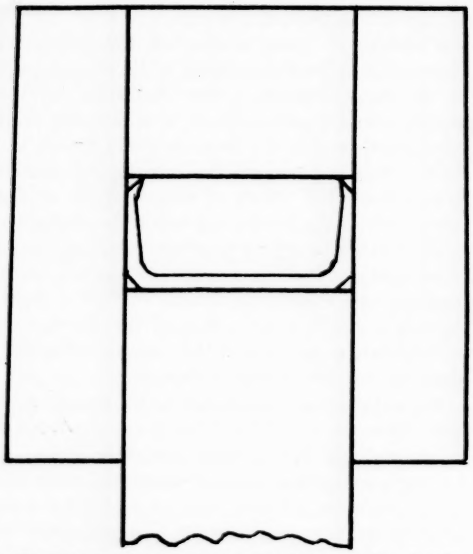

FIGURE 2. Detail of compression sample, showing the sample in the cup shaped indium sheath with the conical closure rings.

machine oil and the conventional hand pump. The feeding pipe passed through a dead weight free piston gauge in series between pump and press. Freedom of flow through the connecting pipe between free piston gauge and press was lowered by plugging the pipe with a wire of diameter only slightly less than that of the pipe. In this way any pulses of pressure originating in the pumping or changing of weights on the gauge were avoided. This was necessary because pressure must increase or decrease monotonically in order to regularize what small friction effects there are and to justify eliminating them by taking the average of readings with increasing and decreasing pressure.

After setting up the apparatus, a preliminary application of the maximum pressure, about 26,500 kg/cm^2, was made in order to consolidate the contents. The initial zero may, depending on the degree of success in getting rid of all voids in the initial filling, be displaced by a considerable amount by this first application, but the piston reading at the first maximum of pressure seldom if ever differed by more than 0.0001 inch from the reading on the second maximum, showing the effectiveness of the preliminary application of pressure in removing all voids and bringing to a steady state. After the seasoning application, pressure was increased in steps of approximately 2,000 kg/cm^2 by the addition of weights to the piston of the dead weight gauge, and the corresponding readings made on the Ames gauge. Within the limits of comfortable operation of the apparatus, there were in general no time effects, but after every increase of pressure there was no creep in piston displacement, at least after the lapse of the 20 or 30 seconds after the piston gauge had reached equilibrium which was necessary before a reading could be made. Thermal effects are of course to be expected after every increase of pressure; the rapid attainment of equilibrium here is a consequence of the small size of the apparatus and its good thermal conductivity. The only point at which there was perceptible creep was at dead zero, where the elastic recovery imparted by the remnants of shape of the charge might result in the gradual development of voids. The dead zero reading was not used in the calculations, the first point being put at about 250 kg/cm^2. The actual process of making the run, increasing and decreasing pressure in steps of 2,000 kg/cm^2 and recording the readings required something of the order of 20 minutes. The rest of the operations of assembly, disassembly, plotting the points, etc. could be done without undue haste, if there were no unusual hitches, so as to make the total time of a run about one and one half hours.

It was intended to make the method differential like its predecessor. At first, measurements on a given substance were compared with blank runs in which the substance was replaced with an equivalent amount of gold, and the compression computed by difference, assuming the compression of gold known. The blank runs showed such a high degree of uniformity, however, that they were eventually discarded, their final function being merely to give the compressive distortion of the carboloy pistons. It turned out that the correction for the change of cross section

of the carboloy core was negligible, so that the final result could be obtained directly from the measured displacement, making one subtractive correction for the shortening of the pistons, another for the compression of the indium sheath, which was known in terms of the weight and the previous measurements of the compression of indium, and a very small correction for the compression of the steel sealing rings which was so nearly constant that it could be incorporated into the correction for the shortening of the pistons. The ratio of the corrected displacement to the initial effective length of the charge then gives at once the fractional change of volume, the relative change of cross section, as just mentioned, being negligible.

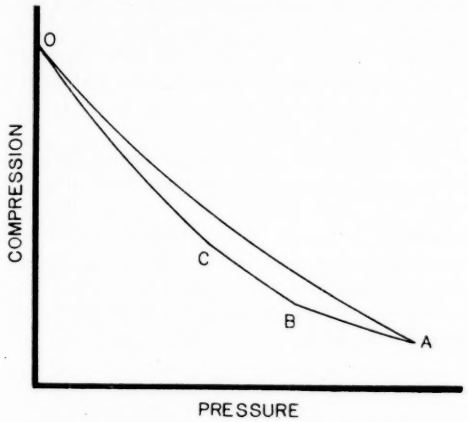

FIGURE 3. Typical compression curve.

The method as just described was arrived at only after a good many exploratory attempts to develop a method for the rapid measurement of the compressibility of solids to high pressures which should exploit the great ease with which rapid measurements of small displacements can be made with the jeweled Ames 0.0001 inch gauge, and the possibility of getting very high stresses in small regions of carboloy apparatus suitably supported by the surrounding parts. It is possible to reach pressures of more than 100,000 kg/cm^2 in carboloy apparatus similar to my shearing apparatus, and to measure the displacements of the pistons in compressing a very thin disc of material. Or, by making the disc somewhat thicker and compressing into a shallow cavity excavated in the face of a carboloy block, greater sensitiveness can be attained, but not such high pressures. None of the many other schemes tried, however, was encouraging from the point of view of accuracy and reproducibility, the distortions in the carboloy corresponding to dishing of the flat face of the piston in the apparatus above being too large a fraction of the total effect.

In Figure 3 is shown a typical curve of displacement versus pressure. The branch with increasing pressure, from O to A, is typically perfectly smooth, but the branch with decreasing pressure consists of three more or less distinct portions. The last part of the return excursion, from C to O, is smooth, and the difference of displacement compared with the ascending branch is approximately proportional to the pressure. The obvious interpretation of this portion is that the difference between the two branches is due to friction, which would be expected to be proportional to pressure, and that the proper mean to take is the arithmetic mean of the displacements with increasing and decreasing pressure. Before reaching C on releasing pressure the readings run through a stretch from B to C in which the difference between readings with increasing and decreasing pressure is approximately constant. The first portion of the return path, from A to B, is merely a connecting link, without special significance, in which the full reverse motion of all parts of the charge gets progressively established. The interpretation of the constant difference between ascending and descending branches between B and C is suggested by my experiments on shearing under pressure.[2] Here it was found that when one solid is forced to slide over another under continually increasing normal pressure, at first the force resisting motion is an ordinary frictional force, arising from surface slip, and is proportional to the normal pressure, but when the normal pressure reaches such a value that the frictional force becomes equal to the stress required to produce internal plastic flow, surface slip ceases, and further relative motion is accomplished by internal plastic flow, the force being to a first approximation, and for not too wide pressure intervals, independent of pressure. This phenomenon was taken to be the interpretation of the constant difference between the two branches from B to C, and consequently the corrected mean curve between B and C is to be taken as half way between the ascending and descending curves, or, in this case, the curve for increasing pressure corrected by a constant additive displacement. Obviously the corrected curve between the pressure at B and the maximum at A

cannot be the mean of the displacements with increasing and decreasing pressure. If the above interpretation is correct, then the corrected curve between B and A is the curve for increasing pressure corrected by the same constant additive term as was used between A and B, neglecting the change with pressure of internal plastic flow stress, which previous work indicates is justified for this range of pressure. The data to be given in the following were obtained by correcting the measurements in this way.

The magnitude of the difference between ascending and descending curves is a strong function of the character of the material being compressed. It is least for soft metals. For indium the maximum difference in displacement between ascending and descending branches was only 0.0001 inch, which is of the order of one per cent of the maximum displacement for this metal. Probably only a small part of this difference arises from internal friction in the indium, but rather arises from friction in other parts of the apparatus. Friction would be expected at the two pistons of the tandem press, and on the outside of the conical block of steel. The pistons of the press were specially treated to reduce friction to a minimum by making the packing thin; the conical steel block was lubricated in the conventional way with 0.002 inch lead foil smeared on both sides with a mixture of graphite, glycerine, and water. An upper limit to the friction from all sources except internal friction in the charge itself would seem from these experiments with indium to be 0.5 per cent. From a minimum difference of 0.0001 inch between ascending and descending branches for indium, the difference might rise to 0.001 inch, ten times as much. Ten times as much does not mean, however, ten times as great proportional error, because the absolute values of displacement were also larger for these substances. It was very seldom that the difference between ascending and descending branches reached as much as 5 per cent of the maximum displacement, or a discrepancy of 2.5 per cent between the mean and either ascending or descending branch. Of course the accuracy of the mean itself should be much higher than this. Even so, it perhaps requires a word of comment as to why there should be as much discrepancy as this. If the indium sheath functions as intended and maintains a hydrostatic pressure on the charge inside it, one might perhaps at first expect no such effect at all, since hydrostatic compression is frictionless and without hysteresis. This applies, however, only to homogeneous material, isotropic or not. The material of these experiments was in most cases highly non-homogeneous, being compressed from powdered or granular material. If the material is non-cubic in its crystal structure, the linear compressibility is in general different in different directions, and the grains change shape under an external hydrostatic pressure. Therefore in a haphazard aggregate of grains of non-cubic material an external uniform hydrostatic pressure produces in general relative motion, with plastic flow and slip of one grain on another and hysteresis. In support of this, the difference between ascending and descending branches was comparatively small for cubic materials, even if they might be of comparatively high mechanical strength. For example, the difference between different branches for NaCl was only about one-third as much as for naphthalene, although to ordinary mechanical stresses the latter is much more deformable than NaCl.

The preliminary work in developing the apparatus and technique of measurement was done with NaCl-clear single crystal stock. The presumptive accuracy of the method can be estimated from a comparison of the results obtained in this apparatus with previous results determined in the pressure range up to 50,000 kg/cm^2, as shown in Table I.

TABLE I

COMPRESSION OF NaCl

Pressure kg/cm^2	$\Delta V/V_0$ Present Measurements	$\Delta V/V_0$ Previous Measurements to 50,000
5,000	.0189	.0192
10,000	.0362	.0365
15,000	.0520	.0523
20,000	.0664	.0664
25,000	.0795	.0798

DETAILED RESULTS

1. *Elements.* Occasion was taken to fill in certain gaps in the compressions of the elements which for one reason or another had not been previously measured to pressures high enough to give an indication of the change of compressibility with pressure. The new values are collected in Table II.

Thallium. This has not been previously measured in the range below 25,000. Thallium crystallizes in the hexagonal system so that a complete description of the behavior under pressure demands a measurement of the linear

TABLE II

COMPRESSION OF ELEMENTS

Pressure kg/cm²	Thallium	Arsenic	Cadmium	$\Delta V/V_0$ Indium	Lead			Ceylon Graphite
					These measurements	From linear compression	Powder	
5,000	.0130	.0119	.0100	.0127	.0110	[.0112]	.0170	.0138
10,000	.0251	.0221	.0194	.0241	.0215	[.0219]	.0323	.0260
15,000	.0367	.0309	.0283	.0347	.0315	[.0321]	.0460	.0366
20,000	.0476	.0385	.0368	.0445	.0411	[.0419]	.0583	.0458
25,000	.0577	.0447	.0449	.0537	.0504	[.0513]	.0718	.0535

compression parallel and perpendicular to the hexagonal axis of the single crystal. I had hoped when making the low pressure measurements to be able to operate with the single crystal, but have not yet successfully prepared single crystals of this metal, the difficulty with the method which I had previously used for the other low melting metals being that thallium attacks the glass container. The volume compression could now, however, be so easily obtained with the new apparatus that it seemed worth while, even if the results would not be complete. The material was some highly purified metal which I had inherited from Professor T. W. Richards, used by him in his measurements of compression in the range up to 500 kg/cm². Thallium is so soft that it could be compressed directly into the carboloy container without the necessity for a sheath of indium. The difference of displacements with increasing and decreasing pressure was at most only 2 per cent of the maximum displacement. The compressibility at atmospheric pressure, extrapolated from these measurements, was found to be 2.7×10^{-7}, against the value of Richards and White[3] of 2.78 in the range up to 500. The agreement is within the sensitiveness of the readings, and again gives presumptive evidence of the reliability of this new method.

Measurements have already been presented[4] for the compression of thallium in the 100,000 apparatus, the range of those measurements being from 25,000 to 100,000. At that time, the fiducial change of volume at 25,000, necessary for the calculations, had not been determined, and it was arbitrarily assumed that the volume decrement was the mean between that of lead and indium, or 0.052. The fiducial volume decrement at 25,000 is now found by direct measurement to be 0.0577. This will permit a re-evaluation of the compressions to 100,000, which will be given in a following paper.

Arsenic. This, like thallium, does not crystallize in the cubic system; it is furthermore known to be highly non-isotropic. The material was highly purified single crystal stock prepared by Dr. W. E. Danforth a number of years ago, the same material as that used in a detailed study of the many anomalies of linear compressibility and electrical resistance of this highly abnormal metal.[5] The sample used in the present measurements was composed of a number of single crystal grains compressed together in haphazard orientation. The regular indium sheath was used. Considerable difference between readings with increasing and decreasing pressure was to be expected because of the mechanical hardness and high non-isotropy. The maximum difference between displacements with rising and falling pressure was 10 per cent of the maximum displacement. The average should be fairly good, because rising and falling curves were smooth, with no trace of the anomolies previously found in the linear compression, which indeed was not to be expected because those anomolies were on too small a scale. The initial compressibility at atmospheric pressure, extrapolated from the present measurements, is 2.5×10^{-6}. This is to be compared with the value 3.2×10^{-6} deduced from my previous measurements of linear compression in different directions, and the value of Richards[6] of 4.4×10^{-6} in the pressure range below 500 kg/cm². The explanation of the latter high value is doubtless the formation of voids because of unequal compressibility in different directions.

Cadmium. This material also does not crystallize in the cubic system, so that a complete description of the phenomena of compression demands a measurement of the linear compression of the single crystal in different directions. The measurement of linear compression, however, encounters an unusual complication, because in the single crystal form there are polymorphic transitions at comparatively low pressures,[7] and on passing through them the single crystal form is lost, so that measurements of

linear compression cannot be carried above the transition pressure. The average volume compression as measured here presents, therefore, only a partial picture, but seemed to be worth while in the absence of other information.

The material was spectroscopically pure, for which I am indebted to Dr. H. M. Cyr of the New Jersey Zinc Co. It was mechanically soft enough so that it could be used without the indium sheath without undue friction. The initial compressibility at atmospheric pressure, extrapolated from the volume decrements given in the table, is 2.06×10^{-6}, which is to be compared with 2.21×10^{-6} obtained indirectly from the measured elastic constants of the single crystal.[7] The anomalies previously found in the linear compression would not be expected to be detectible with the present method.

Indium. The reason for making new measurements on this metal was the continued use of its compression in correcting the other measurements. The material was probably not of specially high purity; it is part of the same stock that has been used in all my other work. The new measurements should be better than any others hitherto made; it has already been mentioned that friction and hysteresis were reduced to a very low value. The deviation of the new values from those last published[8] for the range up to 100,000 kg/cm^2 is not great; at 10,000, 0.241 now against 0.023 previous; and at 20,000, 0.0445 now against 0.045 previous. The new values to 25,000 have afforded the basis for improved measurements to 100,000 which have been communicated in the immediately preceding paper.

Lead. The only previously published values to high pressures[9] reach to 45,000; these measurements were rough, being among the earliest obtained by this general method, before the later refinements had been worked out.

The material was 99,9999 per cent purity lead, which I owe to the kindness of Dr. Phillips, to whom it had been sent by the Federated Metals Corporation, 120 Broadway, New York City. This material is particularly well adapted to the new method because of its mechanical softness. It was used without the indium sheath; the maximum difference between ascending and descending readings was 0.0002 inch. The values now found are to be compared with the previous values in the range to 45,000 as follows: at 10,000, 0.0215 now against 0.023 previous; and at 25,000 0.0504 now against 0.050 previous.

In addition to these values, measurements as yet unpublished were made in 1939 by the method of linear compression with sliding potentiometer wire to 30,000 kg/cm^2, using in the calculations recently redetermined values for the linear compressibility of iron. They should have the highest accuracy that I have yet reached. A more detailed account will be published of this work when I have had opportunity to add more materials, which at present embrace only lead, aluminum, copper, and pure iron from two sources. In the meantime, the results by this method are given in Table II for comparison, enclosed in brackets. The absolute values of the presumably more accurate method are consistently higher than by the method of this paper. It is significant, however, that the rate of decrease of compressibility with pressure by the two methods is the same to the limit of significant figures. It is to be emphasized that these two methods are quite independent of each other.

On the basis of these new measurements the compression of lead has recently been measured up to 100,000; the results are given in the preceding paper.

In connection with other measurements occasion arose to measure the compression of finely powdered lead. It might perhaps be expected, because of the mechanical softness of lead, that virtually perfect compacting would be achieved at these high pressures, and that the compression would be the same as that of the massive metal. This proved to be by no means the case, however. After the first application of 25,000 there was no further perceptible change of volume on the second and third applications. In spite of this, the compression, as shown in Table II, was consistently higher, initially by a factor of 1.54 and at 25,000 by a factor of 1.45. The density at atmospheric pressure of the powder after exposure to 25,000 was 10.74, against 11.34 for the massive pure metal. However, only a small part of the difference between these two densities probably represents voids in the compressed powder. The reason for this statement follows. The compression measurements on the powder were continued in the other apparatus to 100,000. After exposure to 100,000 the density was 10.86. The compression of the powder in the range between 25,000 and 100,000 was sensibly the same as that of the massive metal. It is probable therefore that the pressure of 100,000 was enough to sensibly squeeze out all the voids. The difference between the densities 10.86 and 11.34 is probably to be laid to the account of impurities having

considerable mechanical strength, occluded on the surface of the grains of powder, perhaps oxides. In the present experiments only the difference between 10.74 and 10.86 is to be laid to voids. No simple method of effecting a reconciliation between all the figures just given presents itself, but at any rate we have here a dramatic instance of the very great difficulty of getting good values for the compression of compressed powders even under apparently the most favorable conditions.

Graphite. The only measurements of the compressibility of graphite in the literature were made by Richards and collaborators[11] on graphite from "both artificial and natural sources."

Measurements were now made on three different grades of material. The first of these was massive graphite prepared at Niagara Falls by the Norton Co., highly purified, and subjected before measurement to a further exposure to approximately 3000° C at atmospheric pressure. This material was very porous, the density at atmospheric pressure after a preliminary excursion to 25,000 being only 1.80. Measurements were made on the massive slug, without the indium sheath. Under 25,000 kg/cm² it experienced a volume change of 11.5 per cent, half of this occurring in the first 5,000 kg/cm². In view of the high porosity it will not pay to give the results in greater detail, The results are chiefly valuable in emphasizing the extraordinary degree to which porosity persists after exposure to high pressures, even in materials comparatively weak.

The second material was Acheson flake graphite, compressed to a slug completely filling the apparatus without the indium sheath. After exposure to 25,000 the density was 2.13; the volume change under 25,000 was 7.5 per cent. The behavior was roughly like that of the Norton massive graphite, with elimination of the very compressible part of the curve in the first few thousand kilograms. The friction and hysteresis of both the massive and the Acheson graphite were not excessive, being about that of the average material of these experiments.

The third material was natural single crystal stock from Ceylon, in the form of flat flakes a few square centimeters in surface area and 0.010 to 0.020 inch thick. Discs of 0.25 inch diameter were cut from the flakes with a tubular cutter, and the discs were piled flat into the pressure chamber, without the indium sheath. The density at atmospheric pressure after precompression to 25,000 was 2.23. Results with this material were very satisfactory. Friction and hysteresis were minimal, being no greater than for indium itself. Neither was there any region of abnormally high compressibility at the low pressures, but the internal evidence was that the material is sensibly compact. The volume decrement under 25,000 was 5.35 per cent; the results are given in Table II. The initial compressibility, extrapolated to atmospheric pressure, is 2.92×10^{-6}, to be compared with "not greater than 2.9×10^{-6}" by Richards and collaborators.[11] The compressibility of graphite appears to be about fifteen times as great as that of diamond, not a surprising result in view of the great difference of densities.

2. *Inorganic Salts.*

A. *Univalent Nitrates.* Results have been presented in the preceding paper for the compression of these substances in the complete pressure range up to 100,000 kg/cm². The measurements with the present apparatus up to 25,000 were made primarily to provide the necessary fiducial volume decrement needed before the measurements to 100,000 could be reduced, and also to provide the initial part of the compression curve, the compression of these substances not having been previously measured in any extensive pressure range. In general the materials were the same as have been used in previous investigations of polymorphic transitions under pressure;[12] reference is made to the previous paper for details. The results are given in Table III, to one more significant figure than in the preceding work to 100,000. The values given here are those obtained immediately with the present apparatus, with no attempt to reconcile the measurements in the lower range with those to be reported presently in the higher range.

Apparently the only compressibilities in the literature by other observers for any of the nitrates are by Madelung and Fuchs[13] for $NaNO_3$ and $AgNO_3$. For the compressibility of these in the pressure range 200 to 500 kg/cm² they found 3.75 and 3.60×10^{-6} respectively against the values 3.8 and 3.5 given by extrapolation of the values in Table III. There are also measurements of my own[14] on the linear compression in different directions of the single crystal up to 12,000 kg/cm². The cubic compressibility may be calculated from the linear compression. The initial compressibility is 3.85×10^{-6} against the value 3.8 above. The volume decrement at 10,000 kg/cm² obtained by calculation from the

TABLE III

COMPRESSION OF NITRATES

Pressure kg/cm²	$\Delta V/V_0$						
	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$	$AgNO_3$	$TlNO_3$	NH_4NO_3
2,000	.0074	.0135	.0093	.0103	.0068	.0082	.0117
3,650		.0229					
		.1129					
5,000	.0179	.1185	.0225	.0247	.0165	.0199	.0274
9,500					.0300		
					.0427		
10,000	.0339	.1378	.0427	.0460	.0443	.0377	.0499
15,000	.0482	.1542	.0608	.0645	.0593	.0534	.0688
20,000	.0611	.1682	.0768	.0805	.0725	.0671	.0845
25,000	.0728	.1801	.0913	.0943	.0842	.0790	.0979

measurements on the single crystal is 0.0346 against 0.0339 of the present measurements.

It is of interest to consider the relative compressibility of polymorphic forms at a transition. $AgNO_3$ experiences a transition at 9,500; the data in the table indicate that the low pressure form has a compressibility at the transition point of approximately 2.85×10^{-6}, and the high pressure form at the same point has 3.25×10^{-6}. That is, the compressibility increases on passing through the transition with decrease of volume, a result which appears paradoxical, but which nevertheless is the behavior at the majority of transitions. KNO_3, the only other nitrate with a transition in the present pressure range, shows the opposite behavior. The low pressure form of this is highly compressible, and the compressibility drops rapidly with increasing pressure, from approximately 7.4×10^{-6} at atmospheric pressure to 5.2×10^{-6} at the transition point at 3,600 kg/cm². The compressibility of the high pressure modification at this point is 4.2×10^{-6}, a 20 per cent drop. Above 3,600 the compressibility drops at a slower rate than does that of the low pressure modification.

B. *Certain Halogenates and Perhalogenates.* Previously[14] a study has been made up to 50,000 kg/cm² of the polymorphic transitions of univalent compounds of the types R Hl O_3 and R Hl O_4, where Hl stands for one of the halogens: chlorine, bromine or iodine. Measurements of the compressions of these same compounds are now given here. In general, the materials were the same as used before, left from the previous work, and the previous paper may be consulted for such details as purity. Three of these substances, however, were new: $LiClO_4$, $NaClO_4$, and $KClO_4$. These had been specially purified by Professor K. Fajans, who was interested in their properties from another point of view, and who requested me to measure their compressions. He has discussed the results in another place.[15] The preparation of these three salts offers unusual difficulties, and Professor Fajans exercised unusual precautions to secure high purity and freedom from moisture. They were supplied to me in glass stoppered paraffine covered bottles. The pressure apparatus was set up as rapidly as possible in order to avoid absorption of moisture from the air. The entire time from opening the bottle to complete enclosing in the pressure apparatus and preliminary application of pressure was about 5 minutes; during most of this time the material was partially covered, exposed to air only on edges and corners.

Of these three perchlorates, $LiClO_4$ has a transition not known before in the average neighborhood of 16,400 kg/cm². The transition is very sticky; it does not start with increasing pressure until about 19,000, and runs slowly, probably being completed only just below the top pressure. On decreasing pressure the reverse transition does not start until reaching 13,000. The compression of the low pressure form should be satisfactory, but under the conditions the change of volume on passing through the transition and the compression of the high pressure phase can be expected to be only rough.

The results are given in Table IV. In general, the compression increases on passing from lithium to sodium to potassium to rubidium to caesium, although there is an exception in the relative position of rubidium and caesium in the perchlorates. Analogy, and also experience with the simple halogen compounds of the type NaCl, would lead to the expectation that compression should similarly increase on passing from chlorine to bromine to iodine. This effect, however, is much less marked in these compounds. It is recognizable in the series $NaClO_3$, $NaBrO_3$, $NaIO_3$, but in the perchlorates of sodium, potassium, and rubidium there is a falling off of compression on passing from the chlorine compounds to those of iodine which seems beyond any possi-

TABLE IV

COMPRESSION OF HALOGENATES

Pressure kg/cm²	$\Delta V/V_0$ $NaClO_3$	$KClO_3$	$CsClO_3$	$NaBrO_3$	$AgBrO_3$	$NaIO_3$	KIO_3	NH_4IO_3
2,000	.0069	.0104	.0108	.0071	.0057	.0068	.0068	.0057
5,000	.0165	.0259	.0257	.0171	.0138	.0165	.0161	.0138
10,000	.0307	.1044[a]	.0478	.0320	.0266	.0312	.0298	.0266
15,000	.0431	.1217	.0666	.0450	.0384	.0444	.0417	.0384
20,000	.0542	.1362	.0827	.0567	.0490	.0564	.0522	.0490
25,000	.0644	.1483	.0967	.0673	.0586	.0675	.0619	.0586

[a] Transition at 7,500 with volume decrements .0388 and .0944

COMPRESSION OF PERHALOGENATES

Pressure kg/cm²	$\Delta V/V_0$ $LiClO_4$	$NaClO_4$	$KClO_4$	$RbClO_4$	$CsClO_4$	NH_4ClO_4	$NaIO_4$	KIO_4	$RbIO_4$	NH_4IO_4
2,000	.0078	.0079	.0088	.0102	.0098	.0125	.0078	.0079	.0093	.0081
5,000	.0189	.0191	.0213	.0245	.0232	.0288	.0184	.0190	.0219	.0195
10,000	.0359	.0364	.0404	.0460	.0427	.0519	.0336	.0355	.0400	.0368
15,000	.0509	.0519	.0574	.0647	.0598	.0716	.0463	.0497	.0553	.0524
20,000	.0802[a]	.0659	.0724	.0817	.0750	.0885	.0569	.0617	.0685	.0664
25,000	.0928	.0784	.0854	.0971	.0890	.1031	.0658	.0820	.0809	.0791

[a] Transition at 16,400, with volume decrements .0557 and .0717

ble experimental error. In searching for an explanation, the effect of crystal structure must obviously be taken into account, polymorphism being common, and there being several types of possible structure.

Previous measurements[16] have been made on the linear compression of single crystals of $NaClO_3$ and $NaBrO_3$ in the range up to 12,000 kg/cm.² The initial compressibilities calculated from these measurements are 4.9 and 4.3×10^{-6} respectively, against 3.6 and 3.7 given by extrapolation of the values in Table IV. The discrepancy is much beyond the experimental error of the present method, and the explanation of it is not clear. However, it is probable that the previous measurements should be disregarded; these were made by a new method, which has been applied to only a few substances, and which has never been adequately checked. The method was especially devised to apply to substances which are acted on by kerosene, and employed smaller samples than usual, mounted in a complicated way under the surface of mercury.

3. *Organic Solids.*

A. *Definite Compounds.* A few simple compounds were investigated, with a range of types of composition. They were taken from the regular stock of the Harvard Chemical Laboratory. In spite of the mechanical softness of organic solids in general under atmospheric conditions, the indium sheath was used in all the measurements. This proved to be necessary, the difference between the ascending and descending branches in general being of the same order of magnitude as for the inorganic compounds. This is perhaps not too surprising, because it has already been found that under high pressures such organic compounds as rubber may acquire a high rigidity, greater even than that of mild steel under the same pressure.

The results are collected in Table V. Under the name of each substance is the density assumed in the calculations. This density was obtained from the measurement of the dimensions of the charge after release of pressure and removal from the apparatus. It is likely to be slightly and consistently in error on the small side, because of a slight swelling in volume on removal from the apparatus due to the elastic springing back of voids not crushed completely flat by the high pressure. The assumed density enters the calculation in such a way that, if at some future time better values are obtained for the density of the perfectly compacted material, the relative compressions given in the table may be corrected by multiplying by the ratio of the corrected density to the assumed density. This means that in general the volume compressions given in Table V are probably slightly too low.

Among these organic solid compounds the compression at 25,000 kg/cm²; ranges from 0.1959 for menthol to 0.0901 for dextrose, or by a factor of 2.2. The initial compressibilities of these two substances, extrapolated to atmospheric pressure, are in the ratio 3.5. This is consistent with the

TABLE V

COMPRESSION OF ORGANIC SOLIDS

Pressure kg/cm²	$\Delta V/V_0$														
	Levulose	Dextrose	Dextrin	Starch	Menthol	Naphthalene	Anthracene	Triphenyl Methane	Thymol	Succinic Acid	Anthroquinone	Benzophenone	Amino-Benzoic Acid		
													ortho-	meta-	para-
	1.570	1.467	1.48	1.45	0.923	1.154	1.197	1.106	1.014	1.506	1.398	1.140			
2,000	.0100	.0101	.0203	.0234	.0342	.0309	.0240	.0293	.0235	.0178	.0215	.0296	.0168	.0225	.0235
5,000	.0239	.0239	.0452	.0486	.0701	.0630	.0505	.0598	.0694	.0405	.0453	.0605	.0374	.0425	.0493
10,000	.0445	.0439	.0764	.0794	.1114	.1076	.0842	.0961	.1094	.0705	.0743	.0981	.0644	.0665	.0813
15,000	.0625	.0611	.1004	.1023	.1428	.1281	.1095	.1230	.1380	.0940	.0965	.1255	.0863	.0848	.1054
20,000	.0783	.0763	.1194	.1213	.1702	.1493	.1291	.1437	.1612	.1130	.1146	.1473	.1045	.1004	.1252
25,000	.0923	.0901	.1353	.1387	.1959	.1674	.1460	.1618	.1829	.1290	.1307	.1657	.1203	.1146	.1428

general experience that a compressibility, initially high, tends to drop off more rapidly with increasing pressure.

There is a rough correlation between the compressions and the densities, the least dense compounds being in general more compressible; the correlation is better at high than at low pressures. The correlation is still closer if one plots the compressibility at the upper end of the pressure range. This is shown in Figure 4, in which are

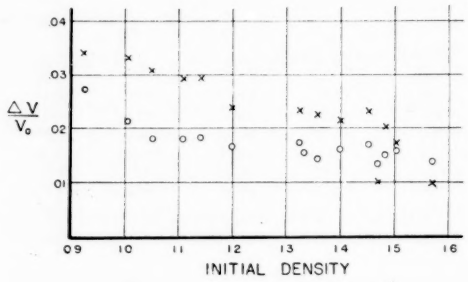

FIGURE 4. The compression of various organic solids as a function of the initial density. The crosses show the relative volume decrements between atmospheric pressure and 2,000 kg/cm², and the circles the relative decrements between 20,000 and 25,000.

plotted as crosses the volume decrement from 0 to 2,000 kg/cm², and as circles the volume decrement between 20,000 and 25,000 kg/cm². The latter set of points lies more nearly on a single curve, and furthermore the curve which best represents the points runs with less change of height from low density to high density. The correlation with density is not materially changed if one plots the final compressibility against the final density instead of against the initial density. In any event, the final compressibility for the denser materials tends to level off to an approximately constant value of 3×10^{-6}. The substances for which there is the greatest failure of correlation between density and compressibility, both at high and at low pressures, are starch and dextrin, the former having abnormally high compressibility and the latter abnormally low.

The reversal of order of densities with pressure in the series of isomeric forms of amino-benzoic acid merits special mention. At atmospheric pressure the densities increase in the order para, ortho, meta, whereas at 25,000 the order is meta, para, ortho, involving a transfer of the meta compound from the head to the foot. The subject is worth further investigation.

It is natural to look for a correlation between the compression at high pressures and the chemical composition. This, however, did not prove especially fruitful. It appears that there is a general tendency for compounds with a large proportion of carbon or of hydrogen in their composition to be relatively compressible, and with a large proportion of oxygen to be relatively incompressible, but further than this no obvious correlation appeared.

B. *Synthetic and Natural Rubbers.* The measurement of these was undertaken at first for the entirely practical purpose of finding some way of predicting which might be expected to function best for high pressure packing on the piston of the apparatus for 30,000 kg/cm². There is considerable difference in the behavior of different rubbers as packings; most rubbers crack at these high pressures, and in some the cracking is so extensive that leak is of frequent occurrence. The cracking probably arises from a combination of circumstances. In the first place, the rubber becomes harder and brittle under pressure exactly as when plunged into liquid air, the phenomenon being essentially a raising of the freezing point with pressure. In the second place, the rubber thus embrittled must be deformed by the unilateral compressive stress arising from the unsupported area principle of the packing sufficiently to neutralize the effect of the uniform volume compression which it would receive under the action of the fluid pressure alone, so that it will again tightly fill the packing space; otherwise leak will occur. This deformation of the embrittled rubber is the probable origin of the cracking. One would expect that, other things being equal, it would be least in those rubbers with the smallest natural volume compressions, and this was the clue followed in the exploration. The distortion necessary to bring the rubber back to fill the packing hole is not small at these pressures. Thus one typical synthetic shows a volume loss of 21 per cent at 25,000 kg/cm²; the corresponding decrease of linear dimensions is 7.6 per cent, which means that the embrittled solid must expand under the unilateral compressive stress by some 8.2 per cent in linear dimensions, preferably without cracking. No rubber has been found entirely free from cracking under these conditions; the best that can be hoped is to find one in which the cracks that do form are not so serious but that they can be sufficiently sealed by the lateral compression.

Ten different specimens of various synthetic rubbers were collected from dealers in the neighborhood of Boston. Measurement disclosed an interesting feature, namely in some of them there was a rather sharp change in the direction of the curve of volume versus pressure, or discontinuity of the second kind, at pressures roughly of the order of 5,000 kg/cm². I had the privilege of discussing this result with Dr. E. Guth, and it seemed to him of sufficient interest to justify examination of specimens whose composition was more definitely known than of the commercial specimens. He accordingly was kind enough to send me 6 representative rubbers of which the compositions are known; the results for four of these are included here and those for the other two will be published later.

The compositions are as follows:

	Hevea Gum	Hevea Tread
SS	100	100
Stand. Micronex	—	52
ZNO (Fast Curing)	3	3
Stearic Acid	4	4
Pine Tar	2	2
Antioxidant	1.5	1.5
S	2.7	2.7
Captax	0.9	0.9
	Butyl Gum	**Butyl Tread**
Butyl B	100	100
Zinc Oxide	5	5
Stearic Acid	3	3
Sulfur	1.5	1.5
Cabot no. 9, Black	—	50
Treads	1	1
Captax	—	0.5

The retraction process and certain other physical properties of the Hevea rubber have been described in recent letters in the Physical Review.[17] Certain properties of the butyl rubber are to be published in a forthcoming number of the Journal of Applied Physics, and were presented at the Rochester meeting of the American Physical Society in the summer of 1944.

The material was cut to the full diameter of the carboloy container and used without the indium sheath. The specimens from Dr. Guth were dimensioned with particular care, being ground to dimensions on one flat face and on the curved face.

In Table VI the compressions for 12 synthetic rubbers and 2 natural rubbers are given. The table also gives the densities at atmospheric pressure calculated from the measured dimensions of the charge at atmospheric pressure, be-

TABLE VI

COMPRESSION OF SYNTHETIC AND NATURAL RUBBERS

Pressure kg/cm²	$\Delta V/V_0$ Duprene	Koroseal no. 89023	Neoprene no. 832	Buna S no. 8774	Ameripol D-7700	Hood 844A	Goodrich D-402	Goodrich D-420	Goodrich D-453	Goodrich D-453	Butyl Gum	Butyl Tread	Hevea Gum	Hevea Tread
2,000	1.589	1.250	1.357	1.376	1.370	1.176	1.193	1.350	1.513	1.309	0.967	1.125	0.950	1.122
5,000	.0302	.0511	.0460	.0465	.0367	.0407	.0422	.0385	.0329	.0432	.0519	.0423	.0535	.0462
10,000	.0615	.0967	.0956	.0872	.0715	.0792	.0837	.0745	.0636	.0842	.0945	.0807	.1017	.0870
15,000	.0898	.1403	.1294	.1238	.1052	.1163	.1194	.1128	.0938	.1208	.1303	.1129	.1422	.1250
20,000	.1198	.1679	.1567	.1493	.1304	.1445	.1454	.1378	.1162	.1480	.1543	.1334	.1697	.1490
25,000	.1301	.1891	.1793	.1715	.1507	.1663	.1670	.1587	.1347	.1692	.1744	.1510	.1929	.1707
	.1462	.2060	.1990	.1903	.1686	.1840	.1847	.1769	.1513	.1862	.1920	.1667	.2116	.1900
Pressure of Discontinuity	3,500		4,800	6,300	4,900		4,800				6,200			6,500
Amount of Disontinuity $\Delta V/V_0$	2.0×10^{-6}		5.3×10^{-6}	3.4×10^{-6}	1.5×10^{-6}		3×10^{-6}				5×10^{-6}			2×10^{-6}
at Discontinuity	.0516		.0939	.1012	.0707		.0851				.1083			.1026
Ratio of Width of Hysteresis Loop to Maximum Displacement	.083	.059	.082	.087	.064	.067	.072	.080	.103	.077	.083	.090	.074	.073

for it had been removed from the pressure apparatus. Thus the expansion on removing from the apparatus, which was a source of error in some of the other densities, was not present in these measurements for rubber, which should be substantially correct. It will be seen that, just as in the case of the solid organic compounds, there is a certain correlation between the compression and the density. This correlation is, however, not so close for the rubbers as for the compounds, as indeed might be expected in view of the fact that there is an artificial factor in the density of the rubbers in the varying degree of loading with carbon black.

The table gives data for the discontinuity of the second kind, that is, the discontinuity in slope, exhibited by 7 of the rubbers. There is listed the pressure of the discontinuity, the volume decrement at the pressure of discontinuity, and the amount of discontinuity in the derivative $\left(\frac{\partial v}{\partial p}\right)_\tau$; in all cases the discontinuity is in the direction of a smaller slope at the higher pressure. No great amount of precision can be claimed for the numerical values of these discontinuities, as is always the case in attempting to measure a discontinuity. In fact, from the point of view of logical rigor, not even the existence of a discontinuity in the mathematical sense can ever be established by physical measurements; it is merely that a discontinuity is the simplest way of reproducing the results to the natural order of accuracy. In any event, there can be no mistaking the striking qualitative difference between the curves for substances like neoprene and Hevea gum. An active imagination would be tempted to find other discontinuities in the curves than those given; only the apparently inescapable ones were listed. One particularly tempting example is afforded by Hood 844A, in which there seems to be rather definitely a discontinuity in $\left(\frac{\partial^2 v}{\partial p^2}\right)_\tau$ near 6,000 kg/cm^2. The physical significance of these discontinuities is probably merely that some rubbers pass more abruptly into the "frozen" condition than do others.

Table VI contains, in addition to the matters just discussed, the width of the hysteresis loop, that is, the ratio of the maximum difference between displacements with increasing and decreasing pressure to the maximum displacement. This varies by a factor of 1.75 fold, somewhat more than does the density or the compressibility. Several factors obviously enter into the width of the loop. There is in the first place the ordinary coefficient of friction of the rubber against the carboloy walls. In the second place there is the internal plastic flow stress within the body of the rubber. In the third place, there is lag, subcooling or superheating, between the ordinary state and the "frozen" state.

Returning to the problem which originally suggested the measurement of the rubbers, it is to be remarked that the single criterion of compression at high pressures did not prove an adequate characterization of the behavior as a high pressure packing. There are other features which are involved in the functioning as packing. Thus, the friction with the steel walls of the pressure vessel must not be too great, and the shearing strength against this frictional drag must be sufficient. Certain of the artificial rubbers which appeared promising from the point of view of volume compression had such a combination of high coefficient of friction and low mechanical strength that when used as packing a vortex ring of rubber was detached from the body of the packing at the periphery and rolled over and over against the steel walls as the plunger advanced. It still remains necessary to make actual trial to determine the suitability for high pressure packing. As yet, exhaustive trial has not been made of the suitability of all the rubbers for high pressure packing, but to date Duprene seems the best for all round use. It happens that Duprene also has the smallest compression.

I am indebted to my mechanic Mr. Charles E. Chase for the skillful construction of the apparatus, and to the Carboloy Company for the carboloy used in this and the preceding paper.

RESEARCH LABORATORY OF PHYSICS,
Harvard University, Cambridge, Mass.

References

[1] P. W. Bridgman, Proc. Amer. Acad. 74, 21–51, 1940.
[2] P. W. Bridgman, Proc. Amer. Acad. 71, 387–460, 1937.
[3] T. W. Richards and J. D. White, Jour. Amer. Chem. Soc. 50, 3290–3303, 1928.
[4] P. W. Bridgman, Proc. Amer. Acad. 74, 425–440, 1942.
[5] P. W. Bridgman, Proc. Amer. Acad. 68, 39, 1933.
[6] T. W. Richards, Jour. Amer. Chem. Soc. 37, 1646, 1915.
[7] P. W. Bridgman, Proc. Amer. Acad. 60, 346, 1925.
[8] Ref. 4, p. 434.
[9] P. W. Bridgman, Proc. Amer. Acad. 72, 207–225, 1938.
[10] P. W. Bridgman, Proc. Amer. Acad. 74, 11–20, 1940.
[11] T. W. Richards, W. N. Stull, F. N. Brink, and F. Bonnet, Jr., Carn. Inst. Wash. Pub. No. 76, p. 39, 1907.
[12] P. W. Bridgman, Proc. Amer. Acad. 72, 45–135, 1937.
[13] E. Madelung und R. Fuchs, Ann. d. Phys. 65, 289–309, 1921.
[14] P. W. Bridgman, Proc. Amer. Acad. 64, 66, 1929.
[15] K. Fajans, Phys. Rev. 61, 543, 1942. There are also two doctoral dissertations, giving other results on $LiClO_4$, prepared under the supervision of Professor Fajans, by Oliver Johnson (December 1942) and Jean Chien-Han Chu (December 1943), at present available only in typewritten form.
[16] Ref. 14, p. 64.
[17] B. A. Mrowca, S. L. Dart and E. Guth, Phys. Rev. 66, 30, 1944; B. A. Mrowca, S. J. Dart and E. Guth, Phys. Rev. 66, 32, 1944; H. M. James and E. Guth, Phys. Rev. 66, 33, 1944.